

VIA EFS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

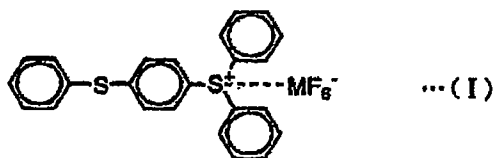
In Re Patent Application of: :
Takashi ITO, et al. :
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Conf. No.: 8148 : Group Art Unit: 1795
: :
Appln. No.: 10/562,098 : Examiner: Anca Eoff
: :
Filing Date: December 21, 2005 : Attorney Docket No.: 9369-114US
: (T37-196236C)
Title: ACTINIC RADIATION-CURABLE STEREOLITHOGRAPHIC RESIN COMPOSITION
HAVING IMPROVED STABILITY

DECLARATION OF TSUNEO HAGIWARA UNDER 37 C.F.R. § 1.132

I, Tsuneo Hagiwara, declare and state as follows:

1. I received a Ph.D. in chemistry from the University of Tsukuba (Japan) in March 1990.
2. Since April 2001, I have been employed by CMET Inc., an assignee of the present application. I have been engaged in the research and development of photoresins for stereolithography.
3. I am a co-inventor of the above-referenced application. I am familiar with the above-referenced application, and in particular with the final Office Action dated March 13, 2009 (Paper No. 20090311). I am submitting the present Declaration to overcome any § 103(a) rejections of claims 1, 3, and 5-10 by demonstrating that resins prepared from compositions containing a photoinitiator for cationic polymerization that comprises a compound having formula (I) below in which M = Sb (antimony) are superior to resins prepared from similar compositions in which M = P (phosphorous). The resins prepared from the antimony-containing compound have higher curing sensitivity so that they can be cured at lower irradiation energy,

and are stronger and more robust than the resins prepared from the phosphorous-containing compound.



The Examiner's Position and the Purpose of the Declaration

4. The Examiner has taken the position that the closest prior to the invention includes U.S. Patent No. 5,776,634 of Ohkuma et al. ("Ohkuma"), WO 02/48101 of Date et al. ("Date"), and U.S. Patent Application Publication No. 2004/0137368 of Steinmann ("Steinmann").

5. In the final Office Action dated March 13, 2009, the Examiner rejected claims 1, 3, 5-6, and 9-10 under 35 U.S.C. § 103(a) as being obvious over Ohkuma in view of Date, relying on U.S. Patent Application Publication No. 2004/0030158 of Date as an English equivalent. The Examiner argued that Ohkuma teaches a photosensitive recording medium composition containing a radical-polymerizable monomer, a cationic-polymerizable monomer, a radical polymerization initiator and a cationic-polymerization initiator. The Examiner argued that the cationic initiator could be represented by formula (I), which would be equivalent to claimed formula (I) when Ar is a phenyl group. The Examiner further argued that specific formula (II) of Ohkuma was equivalent to claimed formula (I) when M is a phosphorus atom. The Examiner acknowledged that Ohkuma does not teach the claimed purity of the cationic polymerization initiator.

6. However, the Examiner argued that Date teaches a method of manufacturing sulfonium salts used as photocationic polymerization initiators for resists. The Examiner further argues that Date discloses the syntheses of (4-phenylthiophenyl)diphenylsulfonium hexafluorophosphate and (4-phenylthiophenyl)diphenylsulfonium hexafluoroantimonate with a

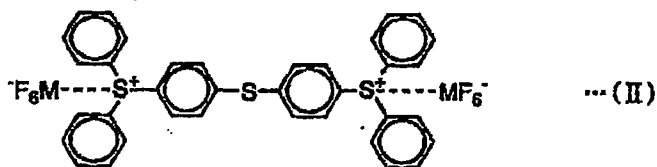
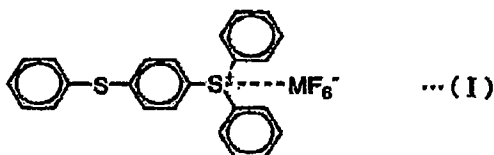
purity of 99%, and further that analyses indicated that the products comprised small amounts of raw materials. The Examiner argued that there is no compound represented by claimed formula (II) in the products described by Date and therefore concluded that the claimed limitations for the quantity of compound of formula (II) are met. The Examiner took the position that it would have been obvious for one skilled in the art at the time of the invention to use the sulfonium salts with a purity of 99% obtained in the process of Date as photocationic polymerization initiators in the composition of Ohkuma since Date specifically indicates this use for such high-purity sulfonium salts.

7. In the final Office Action, the Examiner also rejected claims 7 and 8 under 35 U.S.C. §103(a) as obvious over Ohkuma et al. in view of Date and further in view of Steinmann. The Examiner acknowledged that neither Ohkuma nor Date teaches that the composition comprises an oxetane compound and a polyalkylene ether compound as claimed. However, Steinmann allegedly teaches a radiation-curable composition useful for the production of three dimensional articles by stereolithography comprising, in part, at least one hydroxyl-functional compound and at least one hydroxyl-functional oxetane compound. Accordingly, the Examiner concluded that it would have been obvious to one having ordinary skill in the art at the time of the invention to add at least one hydroxyl-functional compound, such as propylene glycols of various molecular weights, glycerine propoxylated polyether triol and polyethyleneglycols, and at least one hydroxyl-functional oxetane compound, as disclosed by Steinmann, to the composition of Ohkuma/Date in order to obtain a composition with exceptionally high photospeed, low viscosity, low humidity sensitivity, and high temperature resistance since such properties are taught by Steinmann.

8. The purpose of this Declaration is to demonstrate that photoinitiators for cationic polymerization comprising a compound having formula (I) in which M represents different metals, such as Sb and P, are not equivalent. Rather, resins produced from compositions containing the formula (I) compound in which M = Sb are superior in terms of curing sensitivity, strength, and resistance to physical damage than resins produced from compositions containing the formula (I) compound in which M = P. This demonstration will thus overcome the §103(a) rejections of claims 1, 3, and 5-10.

Background and Purpose of the Invention

9. The presently claimed invention is directed to an actinic radiation-curable resin composition for stereolithography that includes a cationic polymerizable organic compound comprising at least one compound having an epoxy group, a radical polymerizable organic compound comprising at least one compound having a (meth)acryl group, a photo initiator for radical polymerization which is sensitive to ultraviolet light, and a photo initiator for cationic polymerization which contains a highly pure (97 weight % or higher) compound represented by formula (I) and less than 3% by mass of a compound represented by formula (II). In formulas (I) and (II), "M" represents an antimony atom and the broken lines represent ionic bonds.



The compound having formula (I) is highly pure to improve the aging stability during operation and the storage stability of the composition. Applicants have determined that the stability of the resin composition may be dramatically improved by increasing the ratio of the compound having formula (I) to the compound having formula (II), that is, preferably substantially excluding compounds of formula (II).

10. In order to demonstrate that resins prepared from resin compositions containing a photoinitiator for cationic polymerization represented by formula (I) in which M = Sb are superior to those prepared from similar resin compositions in which M = P, four resin compositions were prepared: two containing a formula (I) compound in which M = P and two containing a formula (I) compound in which M = Sb. The four compositions were used to form

resins which were analyzed to determine the curing sensitivity and the strength, mechanical, and physical properties of the cured films.

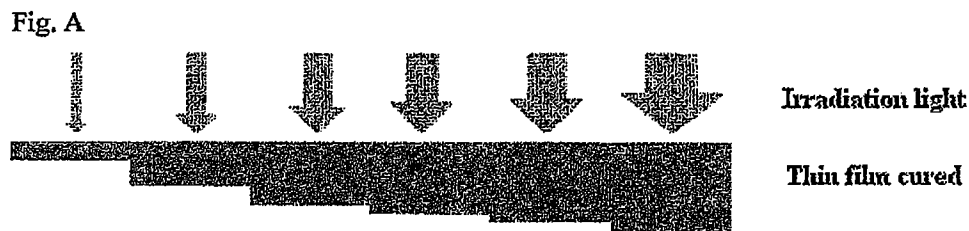
Experimental Procedure

11. Preparation of Resin Compositions. Four resin compositions were produced as described in Examples 1 and 2 of the present application using the components shown in Table 1 below. The four compositions included two compositions ("Additional Example 1(Sb)" and "Additional Example 2 (Sb)") which contained a compound having formula (I) in which M = Sb as a photoinitiator for cationic polymerization, and two compositions ("Additional Comparative Example 1 (P)" and "Additional Comparative Example 2 (P)") which contained a compound having formula (I) in which M = P as a photoinitiator for cationic polymerization. Other than "CPI-101A" and "Photoinitiator including phosphorous", the components listed in the Table are the same materials (same brand, same manufacturer) as described in Examples 1 and 2 of the present application. In the Table, "UVR-6105" is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, "OXT-101" is 3-methyl-3-hydroxymethyloxetane, and "PTMG-2000SN" is polytetramethylene glycol. "CPI-101A" is a photoinitiator for cationic polymerization manufactured by SAN-APRO Ltd which is a 50% propylene carbonate solution of the compound having formula (I) in which M is an antimony atom. This compound has a purity of 99% or higher and is only sold in solution. It was used to prepare the compositions of Additional Examples 1 and 2. The "Photoinitiator including phosphorous" was prepared by dissolving "CPI-110P" (a photoinitiator for cationic polymerization manufactured by SAN-APRO Ltd. in which M in the compound represented by formula (I) is a phosphorous atom, and having a purity of 99% or higher) in propylene carbonate to give a 50% propylene carbonate solution thereof. It was used to prepare the compositions of Additional Comparative Examples 1 and 2.

Table 1: Compositions

	Additional Example 1 (Sb)				Additional Comparative Example 1 (P)				Additional Example 2 (Sb)				Additional Comparative Example 2 (P)			
	30g/100 parts				30g/100 parts				30g/100 parts				30g/100 parts			
Component	Part	Wt%	Additive Amount (g)		Part	Wt%	Additive amount (g)		Part	Wt%	Additive Amount (g)		Part	Wt%	Additive amount (g)	
UVR-6105	1,500	41.27	450.00		1,500	41.27	450.00		1,800	53.73	540.00		1,800	53.73	540.00	
BPO-20E	500	13.76	150.00		500	13.76	150.00		0	0.00	0.00		0	0.00	0.00	
A-BPE-4	500	13.76	150.00		500	13.76	150.00		500	14.93	150.00		500	14.93	150.00	
ATM-4P	400	11.00	120.00		400	11.00	120.00		300	8.96	90.00		300	8.96	90.00	
A-DCP	300	8.25	90.00		300	8.25	90.00		0	0.00	0.00		0	0.00	0.00	
OXT-101	300	8.25	90.00		300	8.25	90.00		300	8.96	90.00		300	8.96	90.00	
PTMG-2000SN	0	0.00	0.00		0	0.00	0.00		300	8.96	90.00		300	8.96	90.00	
I-184	45	1.24	13.50		45	1.24	13.50		60	1.79	18.00		60	1.79	18.00	
CPI-101A	90	2.48	27.00		0	0.00	0.00		90	2.69	27.00		0	0	0.00	
Photoinitiator including phosphorous	0	0.00	0.00		90	2.48	27.00		0	0	0.00		90	2.69	27.00	
Total	3635	100.00	1090.50		3635	100.00	1090.50		3350	100.00	1005.00		3350	100.00	1005.00	

12. Evaluation of Curing Sensitivity. The curing sensitivities of the resins were measured in accordance with the method described in P. Jacobs; *Rapid Prototyping and Manufacturing; Society of Manufacturing Engineers*; 1992 (p. 270). Specifically, the resin compositions were stored in Petri dishes and irradiated with an ultraviolet laser to form thin films. By using six different irradiation energies as shown below in Fig. A, thin films having different thicknesses were prepared. The relationship between the irradiation energy and the thickness cured was obtained by measuring the thickness cured.



When light enters in the depth direction, the strength of the light exponentially decays in accordance with the Lambert-Beer law. Therefore, the logarithm of the irradiation energy is proportional to the thickness of the thin film, which were determined by using a constant-pressure vernier caliper manufactured by Mitutoyo Co., Ltd. The results are tabulated in Table 2 and Fig. B below.

13. Evaluation of Mechanical Strength and Visual Properties. Each composition was used to produce a test piece by stereolithography as described in the specification at page 30. The test pieces were analyzed to determine their tensile and flexural properties in accordance with JIS K7113 and their Shore D surface hardness. The test pieces were also inspected visually. The results are tabulated in Table 3 below.

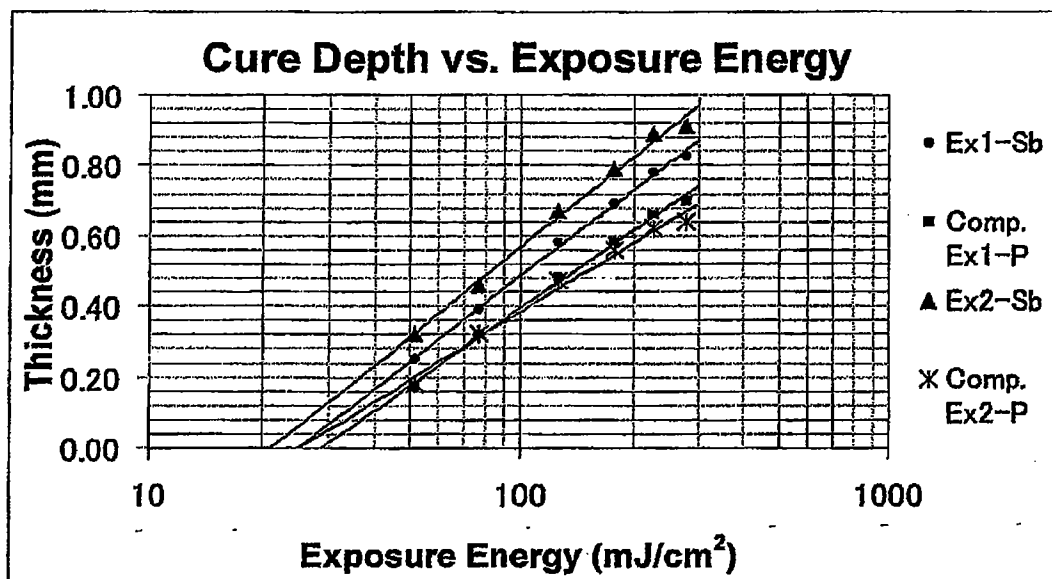
Results and Discussion

14. Results of Curing Sensitivity Evaluation. The results of the evaluation of curing sensitivity are tabulated in Table 2 and depicted graphically in Fig. B.

Table 2: Curing Sensitivity Data

Irradiation Energy (mJ/cm ²)	Thickness cured (mm)			
	Ex. 1(Sb)	Comp. Ex. 1 (P)	Ex. 2 (Sb)	Comp. Ex. 2 (P)
51	0.25	0.17	0.32	0.18
77	0.39	0.32	0.46	0.32
127	0.58	0.48	0.67	0.47
177	0.69	0.58	0.79	0.56
227	0.78	0.66	0.89	0.62
277	0.83	0.7	0.91	0.64
Ec (mJ/cm ²)	24.86	28.69	21.22	25.02
Cured Product	Tough	Fragile	Tough	Fragile

Fig. B.



15. As shown above, at each irradiation energy, the two films prepared using the photoinitiator in which M is phosphorus were thinner than the two films prepared using the

photoinitiator in which M is antimony. This trend may also be seen from considering the graph in Fig. B. The value of the x-intercept on the graph is known as E_c (critical exposure energy), which represents the amount of energy necessary for initiating curing, i.e., achieving gel point. Namely, a smaller value of E_c represents a higher sensitivity. It can be clearly seen from the graph that the sensitivity decreases when using a photoinitiator containing phosphorous. The compositions of Additional Comparative Examples 1 and 2 were thus less sensitive than those of Additional Examples 1 and 2; the comparative compositions would require more energy to achieve the same film thickness.

16. It was observed that the cured films prepared from the resin compositions containing the photoinitiator in which M was antimony (Examples 1 and 2) were tough and easily handled. In contrast, the cured films prepared by using the photoinitiator in which M was phosphorus (Comparative Examples 1 and 2) were weak and easily broken, and thus lacked strength.

17. Results of Mechanical Property and Visual Evaluations. The results from the evaluation of mechanical and visual properties are summarized in Table 3.

Table 3: Mechanical Properties

	Ex. 1	Comp. Ex. 1	Ex. 2	Comp. Ex. 2
Photoinitiator	Sb	P	Sb	P
Tensile Strength (MPa)	49	5.5	45	3.5
Tensile Elongation (%)	6.6	1.7	11.0	28.4
Tensile Modulus (MPa)	1840	353	1920	78.5
Flexural Strength (MPa)	70	13	65	1.7
Flexural Modulus (MPa)	2180	479	1920	49
Shore D surface hardness	86	68	84	39
Color of photocured product	Pale yellow transparent	Colorless transparent	Slightly cloudy	White and opaque
Appearance of Photocured Product	good	Peeling and blemished	good	blemished

18. As shown in Table 3, test pieces prepared from resin compositions containing a photoinitiator in which M was phosphorus exhibited remarkably low strength and modulus: because the reactivity of these comparative compositions was low, the curing reaction did not proceed sufficiently. These materials would thus not be practical for use. In addition, since the surface hardness, strength, and interlayer adhesion of these test pieces were low, surface blemishes and peeling of the cured layer were observed during the stereolithography and post-treatment step, resulting in the observed change of shape and poor appearance.

19. In contrast, the test pieces prepared from resin compositions containing a photoinitiator in which M was antimony exhibited good physical properties and dramatically higher strength and modulus properties. Because these compositions have higher reactivity, the curing reaction proceeded to an appropriate extent and practically useful materials were produced.

Conclusion

20. This Declaration demonstrates the importance of utilizing a photoinitiator containing a compound having formula (I) in which M is an antimony atom when preparing a resin composition. The use of such photoinitiators provides higher curing sensitivity and the ability to perform curing with lower irradiation energy than may be achieved when using a

similar photoinitiator in which M is phosphorous. Further, the use of a phosphorous-containing photoinitiator having formula (I) leads to a resin composition with low reactivity and a cured product with inferior strength, modulus, and other physical properties. Finally, the dramatic difference in properties that is observed when using resin compositions which differ only in the metal element which is contained in the photoinitiator for cationic polymerization has been clearly demonstrated.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that those statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code; and that such willful statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: June 12, 2009

Tsuneo Hagiwara
Tsuneo Hagiwara